Solubility of Isobutane in Two High-Density Polyethylene Polymer Fluffs

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Synopsis

Solubility and rate of desorption of isobutane vapor in high-density polyethylene (HDPE) polymer fluff and a HDPE-hexene-1 copolymer fluff for isotherms between 65.5 and 93.3°C are reported. The data were obtained for pressures to near the vapor pressure of isobutane. Solubilities were correlated using Henry's law, Flory–Huggins theory, and weight fraction activity coefficients. The last approach gave the best correlation of data over the entire temperature and pressure range. The estimated rate of sorption of isobutane is 1.5×10^{-4} mol iC_4H_{10}/g fluff/bar/min over the range studied.

INTRODUCTION

High-density polyethylene (HDPE) polymerization occurs in a hydrocarbon diluent such as hexane or, in some of the newer processes, isobutane. To minimize production costs and maximize the safe handling and storage of the polymer, the diluent must be stripped from the polymer fluff. Stripping unit design requires both equilibrium data and estimates of the rate of desorption.

There have been numerous studies of the solubility of hydrocarbons in polyethylene,[1–5] many of them related to permeability or diffusion studies.[6–11] However, only Santos et al.[3] measured the solubility of isobutane in low-density polyethylene. They used a low-density polyethylene film and studied the range 30–60°C, with pressures ranging between 0.27 and 2.39 bar.

This paper presents solubility data for isobutane vapor in a HDPE polymer and a hexene-1 copolymer as a function of temperature and pressure. The data were obtained at 65.6, 73.9, 82.2, and 93.3°C and at pressures up to 13 bar. The data are correlated using three different approaches. Also, an estimate is given of the rate of desorption.

EXPERIMENTAL

Apparatus

The apparatus was designed so that both rates of sorption and solubilities could be measured. Sorption rates were found by fitting pressure decay curves to a simple, exponential decay equation. The solubility was computed via an isobutane mass balance before and after the pressure decay.

Figure 1 shows a schematic of the apparatus. The sample holder had a volume of 480 cm³ and contained about 200 g sample. Uncertainty in sample weight was ±0.005 g. A 50 μm filter was connected to the sample holder to prevent
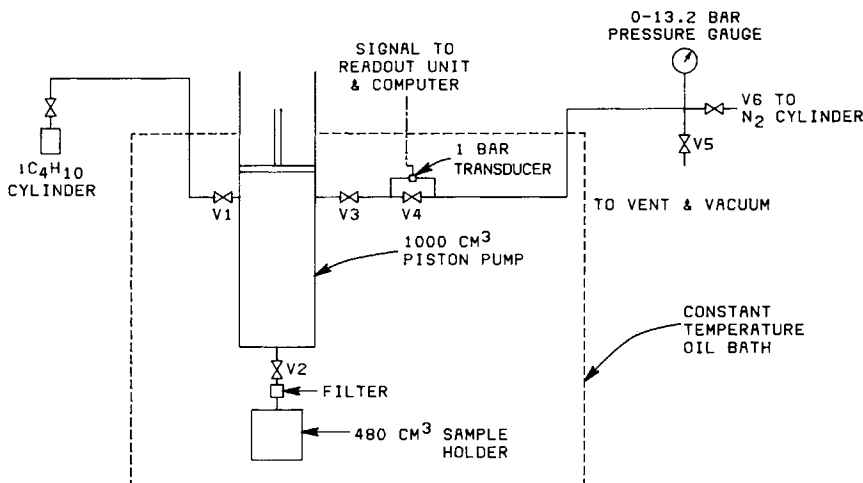
Fig. 1. Schematic of experimental apparatus.

sample loss during rapid depressurization. The Ruska piston pump had a displacement of 1000 cm³. It had a vernier scale which permitted volume readings to 0.01 cm³. A 1-bar differential pressure transducer measured the pressure decay. The reference pressure on the transducer was measured using a 0–13.8 bar (0–200 psia) Heise gauge with 0.034-bar (0.5-psi) graduations.

The sample holder, three quarters of the piston pump, and the pressure transducer were in a well-stirred oil bath kept constant to within ±0.3°C. Temperatures were measured using a total-immersion thermometer. Research-grade isobutane was used in all experiments. The reference side of the transducer was pressurized with dry nitrogen.

Procedure

Each series of runs on an isotherm would start with the fluff sample being evacuated for at least 1 hr to remove residual isobutane. The sample holder was isolated by closing valve V2, and the piston pump was pressurized to 1.45 bar with isobutane. Next, the transducer was zeroed and calibrated at 0.14-bar increments to 0.69 bar. The zeroing procedure was made in a manner to prevent isobutane contamination by nitrogen. After ensuring that the pressure gauge pressure was equal to the pressure in the piston pump, the run was started by opening valve V2. At the end of the run, valve V2 was closed and the volume in the pump decreased until the pressure equaled the initial pressure. The volume change was recorded and the pump returned to the original position for the next run.

Successive runs were made at 3.45 bar in the piston pump and at 1.7-bar intervals to near the vapor pressure of isobutane. Prior to each run the transducer was zeroed and calibrated. In these runs the initial pressure in the sample holder was the final pressure from the previous run.

Isobutane solubility in the fluff was computed by determining the decrease in the number of moles in the vapor phase during a sorption run. The number of moles N_i, in the fluff at the end of run i, was found using

$$N_i = \left(\frac{P}{z}\right)^0 \frac{\Delta V}{RT}\left[\left(\frac{P}{z}\right)_{f,i} - \left(\frac{P}{z}\right)_{f,i-1}\right]\frac{V_v}{RT} + N_{i-1} \qquad (1)$$

where ΔV refers to the change in pump volume and V_v is the void volume in the sample holder; the superscript 0 refers to the initial pressure. The z value was computed at each pressure and temperature using the BWR equation of state, fit to isobutane data by Das et al.[12] For the first run on an isotherm, $P_{f,i-1}$ and N_{i-1} were zero.

The void volume was measured by making low-pressure sorption runs with nitrogen and assuming that it was insoluble in the polymer. This assumption was valid because, for nitrogen, there was no detectable pressure decay similar to those observed for isobutane.

Error Analysis

The total uncertainty in the solubility data is estimated to be 3 and 2% of the reported values for the HDPE polymer and copolymer data, respectively. The copolymer data have a lower uncertainty because of a procedural change in reading pressures at the end of each run.

These uncertainties were estimated by Monte Carlo techniques. Equation (1) was used in the computation along with conservative estimates for the uncertainty in each independent variable. The calculations show that the absolute error in the solubility increased for successive runs of an isotherm. However, the relative error decreased because the solubility increased faster than the absolute error. The 3 and 2% values represent the maximum relative errors.

Based on additional Monte Carlo calculations, it was found that the major source of error in the solubility data was the pressure measurement. The pressure error contributed to over 90% of the total uncertainty in the data.

DISCUSSION

Table I lists the solubility of isobutane in the two fluff samples as a function of temperature and pressure. Table II gives the properties of the two polymer samples. The solubility data were analyzed using (1) Henry's law, (2) Flory–Huggins Theory, and, (3) weight fraction activity coefficients.

Henry's Law

In direct analogy to the solubility of gases in liquids, the solubility of isobutane in the fluff samples is directly proportional to pressure at relatively low pressures. At reduced pressures (defined here as the pressure at a given pressure divided by the vapor pressure of isobutane, P^s, at the same temperature) of 0.25 or less, the simple Henry's law expression applies:

$$\frac{P}{P^s} = Hw \tag{2}$$

where H is Henry's constant and w is the weight fraction of isobutane in the polymer fluff. For the HDPE polymer fluff, H equals 34.5; and for the copolymer fluff, the value is 33.7. Based on 11 points, the average error in (2) for the HDPE fluff is 0.0003 weight fraction. Equation (2) has an average error of 0.0002 weight fraction for the HDPE copolymer fluff based on 10 points. These coefficients apply only in the 60 to 90°C temperature range studied here. Santos et al.[3]

TABLE I
Solubility of Isobutane in Two HDPE Fluff Samples as a Function of Temperature and Pressure

Temperature, °C	Pressure, bar	Solubility, wt %
HDPE Polymer Fluff		
65.6		
	0.97	0.22
	1.03	0.23
	2.74	0.70
	4.55	1.22
	6.20	1.79
	7.91	2.46
	9.13	3.13
73.9		
	1.03	0.24
	2.76	0.65
	4.51	1.06
	6.24	1.55
	7.94	2.12
	9.67	2.77
82.2		
	1.00	0.20
	2.77	0.56
	4.53	0.92
	6.25	1.29
	7.97	1.71
	9.72	2.23
	11.41	2.77
93.3		
	1.01	0.17
	2.82	0.47
	4.57	0.79
	6.29	1.12
	8.01	1.46
	10.75	1.83
	11.47	2.24
HDPE–Hexene-1 Copolymer Fluff		
65.6		
	0.96	0.27
	2.72	0.76
	4.47	1.29
	6.18	1.88
	7.88	2.58
73.9		
	0.97	0.24
	2.74	0.67
	4.50	1.15
	6.23	1.63
	7.93	2.16
	9.62	2.86
82.2		
	0.99	0.21
	2.78	0.58
	4.52	0.97
	6.25	1.38
	7.97	1.82
	9.43	2.21
	11.07	2.77

Table I (*Continued from preceding page.*)

93.3		
	1.01	0.17
	2.81	0.48
	4.56	0.82
	6.29	1.16
	7.98	1.45
	9.60	1.79
	11.25	2.16

isobutane data indicate a temperature dependence on H in the 30 to 60°C range.

Gas solubilities can be correlated at higher pressures by correcting Henry's constant for pressure and by correcting for vapor phase nonidealities. The simplest expression is the Krichevsky–Kasarnovsky equation[13]

$$\ln \frac{f_1}{w_a} = \ln H^\infty + \frac{v^\infty(P - P_2^s)}{RT} \tag{3}$$

where f_1 represents the fugacity of isobutane vapor, w_a is the weight fraction of isobutane in the amorphous phase of the polymer (it is assumed that solutes dissolve only into the amorphous phase of semicrystalline polymers), H^∞ is the infinite dilution Henry's constant, defined as

$$H^\infty = \lim_{w_a \to 0} \frac{f_1}{w_a} \tag{4}$$

TABLE II
Physical Properties of HDPE Samples Used in This Study

	HDPE Polymer (Marlex EMN 6030[a] high-density polyethylene)	HDPE–HEXENE-1 Copolymer (Marlex HHM 5502[a] high-density ethylene– hexene-1 copolymer)
Lot number	05-8-0808	05-8-0807
Nominal density, g/cm³	0.964	0.955
Bulk density, g/cm³	0.42	0.42
Crystallinity, %[b]		
Before solubility measurements	76.2	69.3
After solubility measurements	79.8	72.2
Melt index	3	0.35
Molecular weight		
Weight average	89,600	157,000
Number average	12,400	15,700
Particle size distribution, wt %		
>2000 μm	0.0	0.0
>850 μm	1.2	14.7
>500 μm	19.2	43.4
>280 μm	60.4	34.2
>150 μm	13.5	4.5
<150 μm	5.7	3.2

[a] Trade name.

[b] Measured by DSC.

where v^∞ is the infinite dilution partial molar volume of isobutane in the polymer, and P_2^s denotes the vapor pressure of the polymer which is taken as zero. Figures 2 and 3 show plots of f_1/w_a as a function of pressure for the two polymers. Fugacities were computed using the equation of state given by Das et al.[12] Although the consistency within each isotherm is good, we have no explanation for the apparently anomalous behavior of the 65.6°C isotherm for the HDPE polymer data.

The logarithm of f_1/w_a was fitted against pressure to obtain values of the intercept H^∞. Figure 4 shows these values as a function of temperature. The
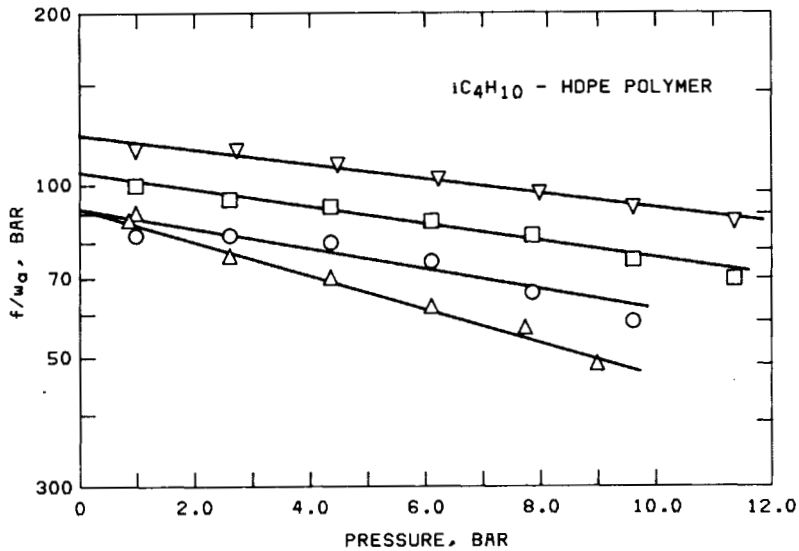

Fig. 2. Solubility of isobutane in HDPE polymer fluff as function of temperature and pressure: (△) 65.6°C; (○) 73.9°C; (□) 82.2°C; (▽) 93.3°C.
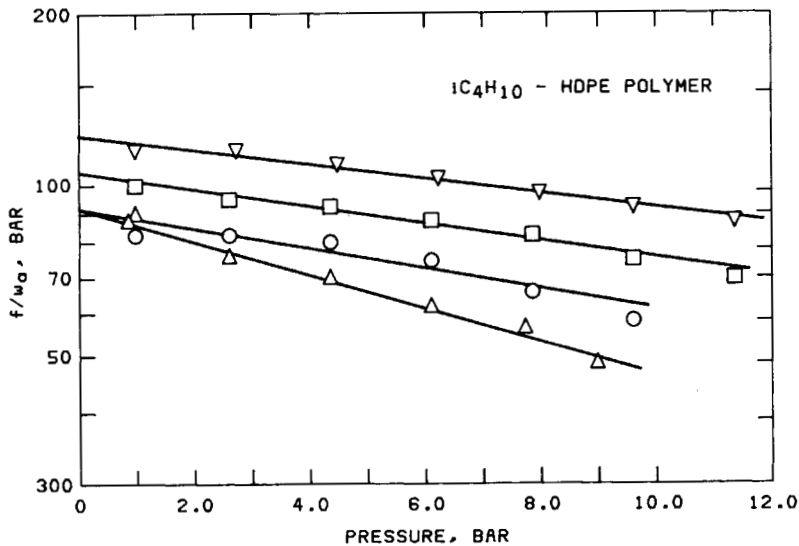

Fig. 3. Solubility of isobutane in HDPE copolymer fluff as function of temperature and pressure: (△) 65.6°C; (▽) 73.9°C; (○) 82.2°C; (□) 93.3°C.
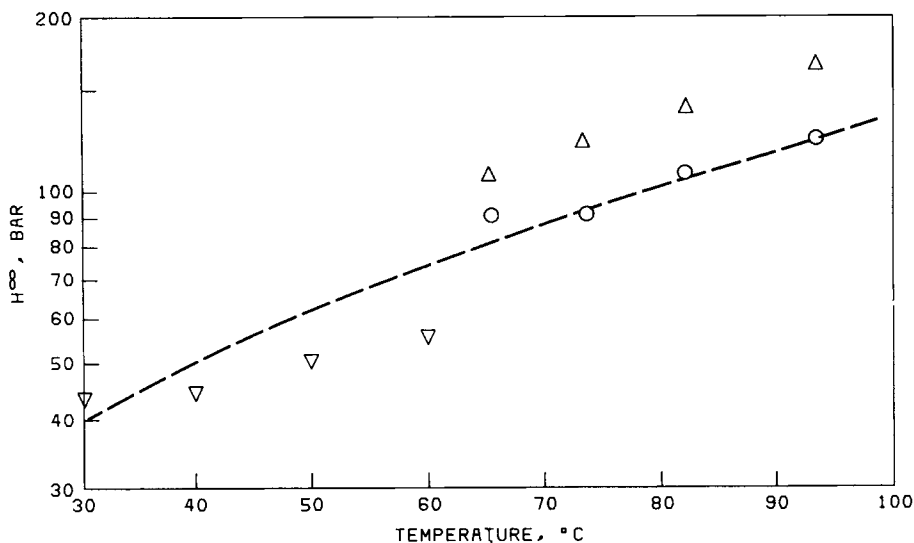
Fig. 4. Infinite dilution Henry's constants as function of temperature: (O) HDPE polymer; (△) HDPE copolymer; (▽) Santos et al.[3]; (- - -) Maloney and Prausnitz correlation.[4]

figure also includes H^∞ values obtained from Santos et al.[3] isobutane data for comparison. Their data were corrected for crystallinity using the reported polymer density and the densities of the amorphous and crystalline phases.[14]

Figure 4 shows values of H^∞ computed from the correlation proposed by Maloney and Prausnitz[4]. Their correlation, which combines Flory–Huggins theory and three-parameter corresponding states, predicts the HDPE polymer H^∞ values very well. However, there is a 30% difference between the values for the polymer and copolymer implying that the addition of hexene-1 within the polymer structure decreases the solubility of isobutane.

The slopes of the lines in Figures 2 and 3 are negative, which implies, from eq. (3), that $\bar{v}^\infty$ is negative. Negative partial molar volumes are physically unrealistic; the negative slopes occur because eq. (3) ignores polymer–solute interactions.

Flory–Huggins Theory

Since the Flory–Huggins theory has been presented before,[13,15] only the appropriate equations are presented here. At thermodynamic equilibrium, the fugacities of the solute in gas and polymer phases must be equal:

$$f_1 = f_1^P \tag{5}$$

where the superscript refers to the polymer phase. Written in terms of measured and computed quantities, eq. (5) becomes

$$\phi_1 P = a_1 \phi_1^s P_1^s \exp\left[\frac{v_1(P - P^s{}_1)}{RT}\right] \tag{6}$$

where ϕ_1 is the vapor phase fugacity coefficient and a_1 is the activity of the solute in the polymer phase. The exponential term represents the Poynting correction to the reference-state fugacity. For these calculations, the saturated liquid volume of isobutane[12] was used for v_1.

Assuming that the polymer molecular weight is large, the activity of the solute in the polymer phase can be expressed using the Flory–Huggins equation

$$\ln a_1 = \ln \Phi_1 + \Phi_2 + \chi\Phi_2^2 \tag{7}$$

where Φ is the volume fraction and χ is the interaction parameter. The volume fraction is based on densities of pure solute and amorphous polymer. For semicrystalline polymer, Rogers[15] suggests that the interaction parameter be expressed as

$$\chi = \mu + \frac{\rho_a v \Phi_2^{-5/3}}{M} \tag{8}$$

where μ is the Flory–Huggins interaction parameter, ρ_a is the density of the amorphous phase, and M is the molecular weight of amorphous polymer between crystalline crosslinks.

Figures 5 and 6 show χ as a function of $\Phi_2^{-5/3}$ for the two polymers. The 73.9°C isotherm data were omitted for clarity's sake. Based on these plots, eq. (8) appears valid only at values of Φ_2 greater than 0.9. The values of χ for isobutane-free polymer (i.e., $\Phi_2 = 1$) decrease with increasing temperature, but the temperature dependence for the copolymer is much less than for the polymer.

A similar analysis of Santos et al.[3] isobutane data indicates that over the concentration range of their work ($\Phi_2 > 0.88$), χ was independent of concentration and decreased from 0.95 to 0.75 with increasing temperature.
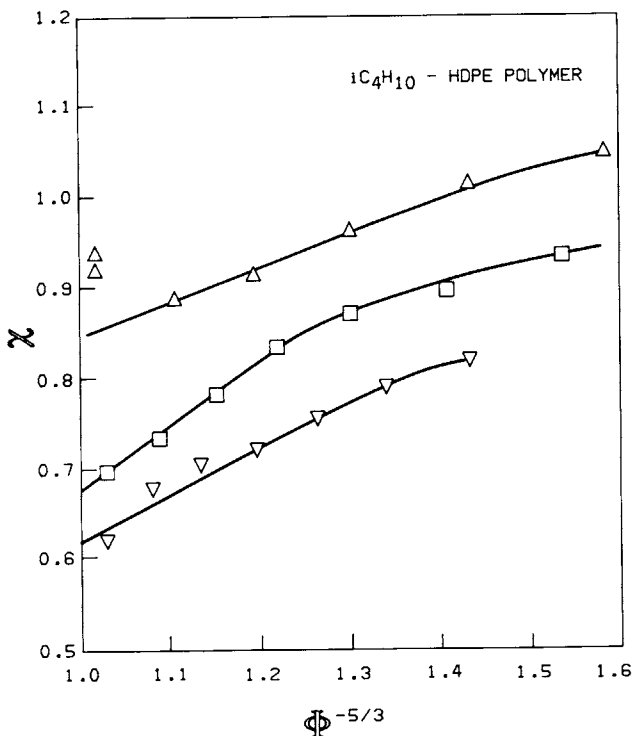

Fig. 5. Plot of interaction parameter vs. $\Phi_a^{-5/3}$ for HDPE polymer fluff at various temperatures: (△) 65.6°C; (□) 82.2°C; (▽) 93.3°C.
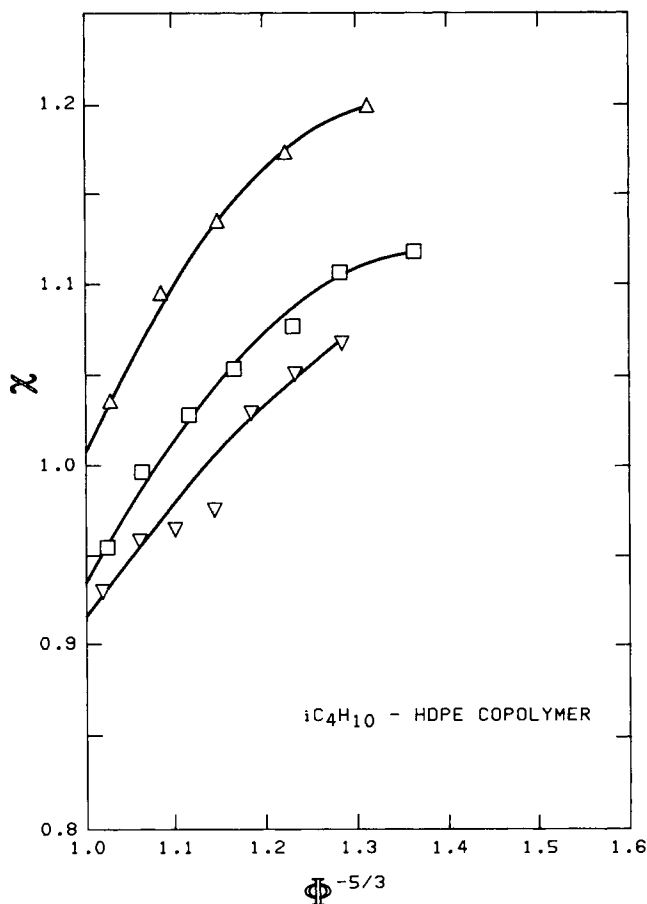
Fig. 6. Plot of interaction parameter vs. $\Phi_a{}^{-5/3}$ for HDPE copolymer fluff at various temperatures: ($\triangle$) 65.6°C; ($\square$) 72.2°C; ($\triangledown$) 93.3°C.

Weight Fraction Activity Coefficients

If we define the activity coefficient for the solute in the polymer phase in terms of weight fraction,

$$\Omega = \frac{a_1}{w_a} = \frac{\phi_1 P}{(w_a \phi_1^s P_1^s)} \exp\left[\frac{-\upsilon(P - P_1{}^s)}{RT}\right] \tag{9}$$

where Ω is the weight fraction activity coefficient. Figures 7 and 8 show Ω as a function of w_a for the two polymers. The isobutane data of Santos et al.[3] are included for comparison.

We fit the activity coefficient to

$$\Omega = \Omega^\infty + bw_a \tag{10}$$

Values of Ω^∞ and b are listed in Table III for the two polymer samples.

For comparison, Figure 7 includes activity coefficients obtained from Santos et al.[3] isobutane data. Although their data give values in the same range as those of the present work, their values show a much stronger temperature dependence
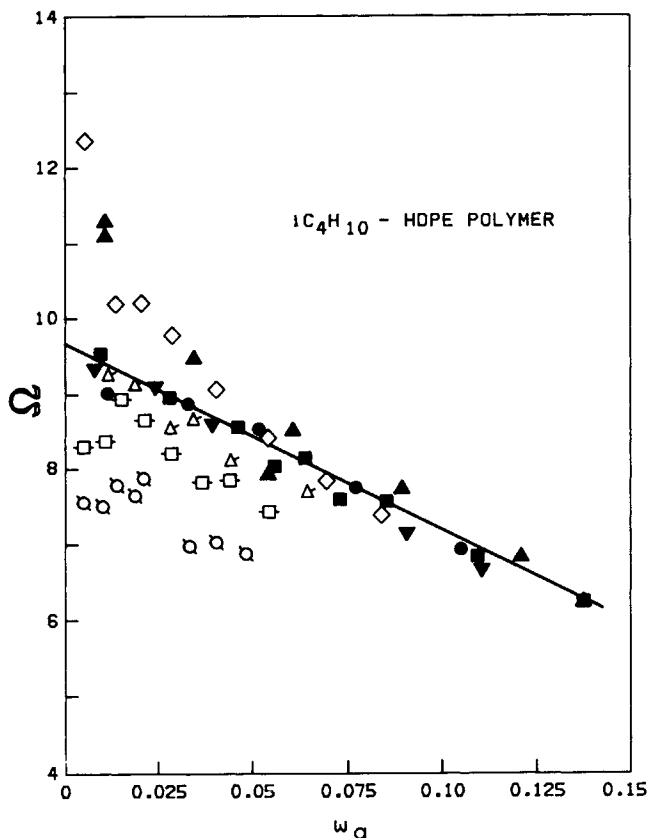
Fig. 7. Weight fraction activity coefficient vs. composition for HDPE polymer fluff; (—) eq. (10): (▲) 65.5°C; (●) 73.9°C; (■) 82.2°C; (▼) 93.3°C.   Santos et al.[3]: (◇) 30°C; (△) 40°C; (-▱-) 50°C; (ⵁ) 60°C.

TABLE III
Coefficients for Equation (10) ($\Omega = \Omega^{\infty} + bw_a$)

	HDPE polymer	HDPE–hexene-1 copolymer
Ω^{∞}	9.66	12.80
99% Confidence interval[a]	0.05	0.04
b	−24.39	−43.33
99% Confidence interval[a]	0.63	0.64
Correlation coefficient (R^2)	0.96	0.99

[a] Based on 23 degrees of freedom.

but about the same concentration dependence.   We have no explanation for the marked temperature dependence differences between the two sets of data.

Rates of Sorption

Estimates of the rate of sorption of isobutane into the polymer fluff were obtained by reducing pressure decay data obtained during the solubility runs. Rates of sorption were found by fitting pressure decay curves to

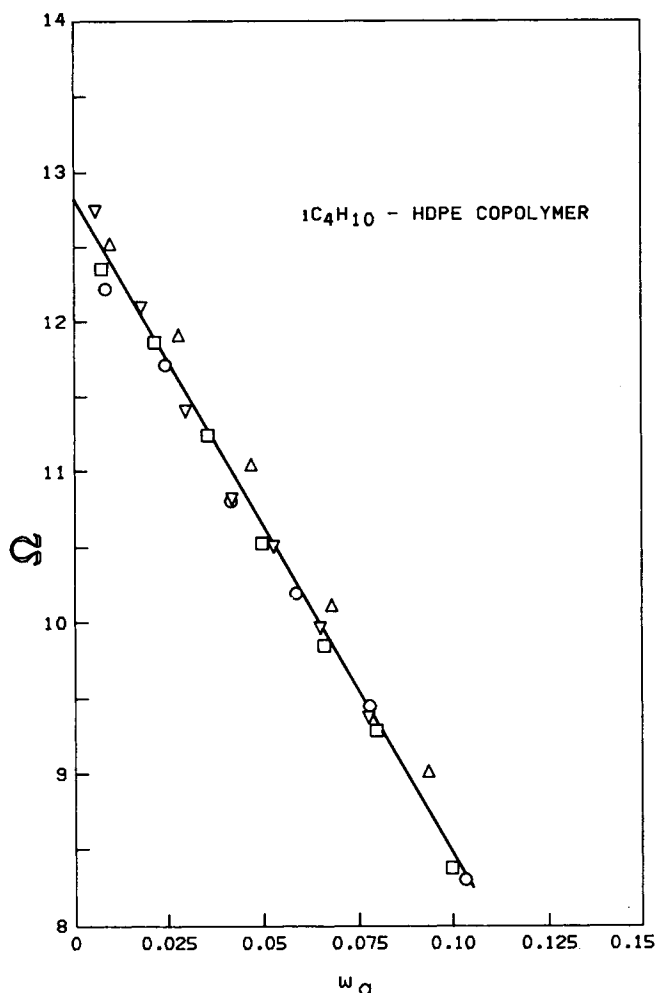$$P = P_f + (P_s - P_f) \exp\left(\frac{-kWzRT}{V}\right) \tag{11}$$

Fig. 8. Weight fraction activity coefficient vs. composition for HDPE copolymer fluff; (—) eq. (10): (▲) 65.5°C; (●) 73.9°C; (■) 82.2°C; (▼) 93.3°C.

where P, P_f, and P_s denote the instantaneous, final, and initial pressures, respectively; k, W, and V represent the rate of sorption, weight of polymer, and volume of gas phase, respectively. Obtaining k from eq. (11) requires nonlinear regression because both k and P_f must be fit. We found a strong correlation between the two parameters, especially at higher pressures, which introduces a large uncertainty in k. Over the temperature and pressure range studied, we found an average value of $1.5 \times 10^{-4} \pm 50\%$ mol iC_4H_{10}/g fluff/bar/min. We verified experimentally that the rates of sorption and desorption are equal for these polymers in the range considered.

CONCLUSIONS

A relatively simple experimental method was used to measure both gas solubility and rates of sorption of gases into polymer fluffs. Based on an analysis of our solubility data we found that:

(1) Gas solubility is proportional to pressure for pressures less than 0.25 times the saturation pressure.

(2) Maloney and Prausnitz[4] correlation predicts Henry's constant for the HDPE polymer but not for the copolymer.

(3) Rogers[15] extension of Flory–Huggins theory to semicrystalline polymers is valid for polymer volume fractions greater than 0.9.

(4) Weight fraction activity coefficients are nearly temperature independent; they provide the best means for estimating gas solubility over the temperature and pressure range considered.

A comparison of our data with the isobutane data of Santos et al.[3] shows marked differences in solubility and in temperature dependence of solubility. This suggests that the data analysis presented here has neglected important physical differences in the two polymers.

Analysis of the pressure decay data indicates that the rate of desorption of isobutane from polymer fluff is roughly 1.5×10^{-4} mole iC_4H_{10}/g fluff/bar/min. This means that it takes about 1 min to decrease the isobutane content in the fluff from the initial value to a value equal to the equilibrium content plus 10% of the difference between the initial and equilibrium concentrations. However, because of the large uncertainty in the data, the effect of temperature, pressure, and type of fluff could not be determined.

Notation

a_1	activity of isobutane in polyethylene polymer
b	slope of activity coefficient weight fraction line, eq. (10)
f_1	fugacity of isobutane, bar
H	dimensionless Henry's constant in eq. (3)
H^∞	infinite dilution Henry's constant, bar
k	sorption rate constant, mol iC_4H_{10}/g fluff/bar/min
M	molecular weight of polymer crosslinkage
N	moles of isobutane contained in the fluff
P	pressure, bar
R	gas constant, l.-bar/K/mol
T	absolute temperature, K
t	time, min
V	volume, liters
V_v	void volume
v	partial molar volume, cm^3/mol
W	weight of polymer sample, g
w	weight fraction
w_a	weight fraction in amorphous phase
z	compressibility factor

Greek Letters

μ	Flory–Huggins interaction parameter
ρ_a	density of amorphous phase, g/cm^3
Φ	volume fraction
ϕ	fugacity coefficient, bar
χ	interaction parameter
Ω	weight fraction activity coefficient

Superscripts

p	polymer phase
s	saturation conditions
0	initial conditions
∞	property at infinite dilution

Subscripts

a	amorphous phase
f	final condition
i	run index
s	initial condition
1	solute
2	polymer (amorphous phase only)

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